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DESCRIPTION

A1 ~~METHOD OF PRODUCING GLASS~~
~~METHOD OF PRODUCING GLASS ARTICLE~~
~~OPTICAL FIBER GLASS PREFORM~~
~~AND GLASS BASE MATERIAL FOR OPTICAL FIBER~~

(C) Making a fiber preform by heating a preform that has temperatures from 1000°C to 1400°C inclusive.

Technical Field

The present invention relates to a large high-quality glass article, and to a method for manufacturing the same. Specifically, the present invention relates to an optical fiber glass preform which is long and has little variation in outer diameter, and to a method for manufacturing the same.

Background Art

A glass article such as a photo-mask glass preform, optical fiber glass preform, etc., is manufactured by heating at a high temperature to vitrify a soot preform synthesized by a vapor phase synthesis method such as the vapor phase axial deposition (VAD) method, the outside vapor deposition (OVD) method, etc., in a vacuum or in a reduced-pressure atmosphere in a furnace. In order to obtain a high-quality glass article, residual bubbles in the glass preform must be avoided as much as possible and the outer diameter of the preform must be uniform. For these purposes, a method in which the heating and vitrifying step is divided into three distinct steps so that the temperature in each step can be appropriately controlled is proposed (Japanese Unexamined Patent Application Publication No. 6-256035). In this method, a

heating process includes a first heating step of removing the gas remaining in the soot preform, a second heating step of heating at a temperature higher than the heating temperature of the first heating step and lower than a vitrification temperature of the soot preform so as to effect thermal shrinkage, and a third heating step of vitrifying the soot preform at a vitrification temperature. Also, in the second heating step, a heating element for heating the soot preform is divided into several segments in the vertical direction so as to allow independent temperature control in each segment. By setting the temperature of the lower heating segment higher than the temperature in the upper heating segment, variation in the outer diameter of the glass article in the longitudinal direction thereof can be minimized.

Recently, in view of the need for mass production and efficiency in the manufacturing process, a method for manufacturing a high-quality optical fiber preform having a length of 1000 mm or more (which is free of residual bubbles and having little variation in the outer diameter in the longitudinal direction) by using a large soot preform has been desired.

The present inventors have noticed a problem that the variation in outer diameter in the longitudinal direction is increased when an optical fiber glass preform having a length of 1000 mm or more, which is significantly affected by the weight thereof, is treated at a high temperature such as that in the third heating step (1490°C to 1600°C).

The present inventors also noticed a problem in that when the vitrification temperature is lower than 1490°C, and when the amount of

heating time is 1 hour or less, vitrification of the soot preform is difficult and both ends of the soot preform include unsintered portions (imperfectly vitrified portions).

Disclosure of Invention

An object of the present invention is to provide a manufacturing method through which a large high-quality glass article having uniform outer diameter in the longitudinal direction can be manufactured from a large soot preform.

A first aspect of the present invention relates to a method for manufacturing a glass article having a length of 1000 mm or more, comprising a first heating step of inserting a soot preform synthesized by a vapor phase synthesis method into a furnace in a vertical direction and heating to a temperature lower than a vitrification temperature in a vacuum or in a reduced-pressure atmosphere so as to remove gas remaining in the soot preform while effecting thermal shrinkage, and a second heating step of heating the soot preform to a vitrification temperature so as to complete vitrification, wherein, during the second heating step, the temperature at the surface of the soot preform is controlled to be in the range of 1400°C to 1480°C and is maintained thereat for a predetermined period of 70 minutes or more, and wherein a step of cooling the glass article is provided subsequent to the second heating step.

A second aspect of the present invention relates to a method for

manufacturing a glass article according to the first aspect of the present invention, wherein the first heating step has a degassing step of removing the gas to a predetermined vacuum level of 10 Pa or less at a temperature in the range of 1000°C to 1300°C.

A third aspect of the present invention relates to a method for manufacturing a glass article according to the first aspect of the present invention, wherein the first heating step has a degassing step of removing the gas to a predetermined vacuum level of 10 Pa or less at a temperature in the range of 1000°C to 1300°C and a thermal shrinking step of heating to a temperature in the range of 1300°C to 1400°C at a predetermined vacuum level of 10 Pa or less.

A fourth aspect of the present invention relates to a method for manufacturing a glass article according to the first aspect of the present invention, wherein the furnace is provided with a heater having a plurality of segments whose temperatures are independently controllable in the longitudinal direction such that the temperature of the soot preform can be controlled correspondingly in a plurality of parts in the longitudinal direction.

A fifth aspect of the present invention relates to a method for manufacturing a glass article according to the first aspect of the present invention, wherein, during each of the heating steps, the temperature at a furnace tube which isolates the soot preform from a heaters is measured and the temperature in each step is controlled based on the measured values.

A sixth aspect of the present invention relates to a method for

manufacturing a glass article according to the first aspect of the present invention, wherein the soot preform is a composite preform comprising a transparent glass rod and a porous glass portion formed around the glass rod.

A seventh aspect of the present invention relates to a method for manufacturing a glass article according to the first aspect of the present invention, wherein, during the second heating step, the temperature at the surface of the soot preform is gradually or stepwise increased from the upper section toward the lower section.

An eighth aspect of the present invention relates to an optical-fiber glass preform having a length of 1000 mm or more and formed by heating a soot preform which is a composite preform comprising a transparent glass rod and a porous glass portion formed therearound and which has a predetermined outer diameter, so as to vitrify the porous glass portion so that the variation in the outer diameter in the longitudinal direction of the vitrified glass preform is within ±2% relative to the median in the longitudinal direction of the outer diameter.

Brief Description of the Drawings

Figure. 1 is a schematic diagram explaining the structure of a vacuum sintering furnace employed in Examples.

Figure. 2 is a graph showing a variation in outer diameter in the longitudinal direction of the optical fiber preform manufactured in Example 1 and Comparative Example 1.

Figure. 3 is a mimetic diagram showing a state of temperature control in Example 3.

Best Mode for Carrying out the Invention

A soot preform obtained by a vapor phase synthesis method such as the VAD method, or the OVD method, etc., is heated in a vacuum or in a reduced-pressure atmosphere during the first heating step so that the gas remaining in the soot preform is eliminated and the soot preform is thermally shrunk. During this step, it is preferable that the gas be removed to a predetermined vacuum level of 10 Pa or less at a temperature in the range of 1000°C to 1300°C and that a thermal shrinking step be then performed at a predetermined vacuum level of 10 Pa or less at a temperature in the range of 1300°C to 1400°C.

Subsequent to the first heating step, the soot preform is heated to a temperature in the range of 1400°C to 1480°C for 70 minutes or more during the second heating step so as to complete vitrification. By setting the heating temperature to the range of 1400°C to 1480°C, the temperature being lower than a vitrification temperature in the conventional art, elongation of the soot preform by the weight thereof is reduced. In such a case, both end portions of the soot preform, the portions at which the temperature is likely to be lower, may not be vitrified completely; however, by setting the heating time to a predetermined time of 70 minutes or more, the both ends of the soot preform can be completely vitrified. Accordingly, by setting a low vitrification

temperature, variations in the outer diameter of the preform in the longitudinal direction may be within a range of ±2% relative to a median of the outer diameter in the longitudinal direction.

Preferably, the furnace used in the present invention is provided with a heater having a plurality of segments whose temperatures are independently controllable in the longitudinal direction such that the temperature of the soot preform can be controlled correspondingly in a plurality of parts in the longitudinal direction. In this manner, even when a long soot preform is heated, the temperature at a portion which suffers from elongation and the temperature at a portion which suffers less from elongation may be appropriately controlled.

Preferably, when an upright furnace in which the soot preform is inserted in the vertical direction is employed, the temperature at the surface of the soot preform is gradually or stepwise increased from the upper section toward the lower section.

In vitrifying the soot preform, in order to isolate the soot preform from a furnace heater, the soot preform is inserted into a furnace tube comprising carbonaceous material, etc., provided between the soot preform and the heater.

Temperature control during the first and second heating steps is performed by measuring the temperature at the surface of the soot preform by using a thermal sensor such as a radiation pyrometer and controlling the output of the heater based on the measured values. The temperature at the surface of the soot preform is approximately the same as the temperature of

the furnace tube in most cases. Since the temperature at the furnace tube is easier to measure, the output of the heater may be controlled based on the values determined in this way.

EXAMPLES

Hereinbelow, the present invention is more specifically described by way of examples.

(Example 1a)

A soot preform comprising pure silica synthesized by the VAD method was vitrified according to the method of the present invention using a vacuum sintering furnace shown in Fig. 1. In the vacuum sintering furnace shown in Fig. 1, reference numeral 1 denotes a soot preform, reference numeral 2 denotes a vacuum sintering furnace main body, reference numeral 3 denotes a furnace tube, reference numeral 4 denotes a heater, reference numeral 5 denotes an inert gas supply unit, reference numerals 6 and 7 denote flow meters for the inert gas supplied into the furnace tube 3 and the furnace main body 2, ~~respectively, reference numerals 8 and 9 denote pipes for~~ respectively, reference numerals 9 and 8 denote pipes for supplying inert gas into the furnace tube 3 and the furnace main body 2, respectively, reference numerals 10 and 11 denote vacuum pumps for reducing the pressure in the furnace, reference numerals 12 and 13 denote pipes for evacuating the furnace main body 2 and the furnace tube 3, respectively, reference numeral 14 denotes a supporting rod for supporting the preform 1, reference numeral 15 denotes an upper cover, reference numeral 16 denotes monitoring hole for

measuring the surface temperature of the preform 1, which extends toward the furnace tube 3, reference numeral 16' denotes monitoring hole for measuring the temperature at the furnace tube 3, reference numeral 17 denotes a pyrometer for measuring the surface temperature of the preform 1, reference numeral 18 denotes a pyrometer for determining a temperature at the furnace tube 3, reference numeral 19 denotes a temperature control device, and reference numeral 20 denotes a traverse mechanism. Means for supplying and evacuating gas may be provided for both the furnace main body 2 and the furnace tube 3 as in the drawing, or for either thereof. In the pipes 8, 9, 12, and 13, valves (not shown in the figure) are provided so that evacuation (pressure reduction) or gas supplying may be carried out by controlling these valves. The pyrometer 18 is connected to the temperature control device 19, though this is not shown in the figure.

The soot preform 1 having an outer diameter of 200 mm, a weight of 30 kg, and an effective length of 1500 mm was synthesized by the VAD method and was used. While maintaining the temperature in the vacuum sintering furnace at 400°C, the soot preform 1 was inserted into the furnace tube 3, the furnace was hermetically sealed with the upper cover 15, and the pressure in the furnace was reduced to 10 Pa. In this state, the surface temperature of the entire soot preform 1 was increased to 1300°C at a rate of 10°C/min and was maintained thereat for 70 minutes so that the gas remaining in the soot preform 1 was thoroughly degassed (degassing step).

The surface temperature of the soot preform 1 was then increased at a

rate of 5°C/min to 1350°C and was maintained thereat for 50 minutes (thermal-shrinking step).

The surface temperature of the soot preform 1 was then increased at a rate of 5°C/min until the surface temperature of the entire soot preform 1 reached 1420°C. The temperature was maintained thereat for 100 minutes to complete vitrification (vitrification step).

Then heating by the heater was discontinued so as to decrease the temperature and to cool the glass article (cooling step), and the product was removed at 600°C.

The size of the obtained glass article was measured and the results showed that the glass article was of superior quality and had little variation in outer diameter, i.e., the outer diameter over the entire effective length of 1400 mm was 90 ±0.5 mm (outer-diameter variation rate was ±0.56%).

(Example 1b)

Instead of the soot preform 1 of Example 1a, a composite preform having the same size as that in Example 1a, the composite preform which had a SiO_2 porous glass layer formed, by using VAD method, around a transparent glass rod having a central portion with a high refractive index doped with Ge and having a pure SiO_2 layer around the central portion, was used. The vitrification was performed as in Example 1a and satisfactory quality was also achieved.

(Example 1c)

A soot preform 1 having an outer diameter of 300 mm, an effective

length of 1500 mm, and a weight of 60 kg was used. As in Example 1a, the degassing step and heating step were performed. The surface temperature of the soot preform 1 was then increased at a rate of 5°C/min until the surface temperature of the entire soot preform 1 reached 1420°C. Then the temperature was maintained thereat for 180 minutes for vitrification.

The obtained glass article was measured and the results showed that the outer diameter was 150 ±1.2 mm (outer-diameter variation rate ±0.6%) over the entire effective length of 1400 mm, achieving high quality.

(Comparative Example 1a)

A soot preform 1 having the same size as that used in Example 1a was vitrified using the same equipment under the conditions below. That is, while maintaining the temperature in the vacuum sintering furnace at 400°C, the soot preform 1 was inserted into the furnace tube 3, the furnace was sealed with the upper cover 15, and the pressure in the furnace was reduced to 10 Pa. In this state, the surface temperature of the entire soot preform 1 was increased to 1300°C at a rate of 10°C/min and was then maintained thereat for 60 minutes so that the gas remaining in the soot preform 1 was thoroughly degassed (degassing step).

The surface temperature of the soot preform 1 was then increased at a rate of 5°C/min to 1350°C and was maintained thereat for 50 minutes (thermal-shrinking step).

The surface temperature of the soot preform 1 was then increased at a rate of 5°C/min until the surface temperature of the entire soot preform 1 was

1500°C. The temperature was maintained for 60 minutes to complete vitrification (vitrification step). Then heating by the heater was discontinued so as to allow the temperature to decrease, and the product was removed at 600°C. The size of the obtained glass article was measured and the results showed a large variation in outer diameter, i.e., the outer diameter over the entire effective length of 1400 mm was 90 ±4.5 mm (outer-diameter variation rate ±5%).

(Comparative Example 1b)

A soot preform 1 having the same size as that used in the Example 1c was used and was vitrified under the same conditions as those in Comparative Example 1a. The size of the obtained glass article was measured and the results showed a large variation in outer diameter in the longitudinal direction, and the outer diameter over the entire effective length of 1550 mm was 150 ±5.0 mm (outer-diameter variation rate ±3%).

The results of Example 1a and Comparative Example 1a are shown in Table 1. The dependence of the outer diameter variation on the longitudinal direction in these examples is shown in Fig. 2. During the second heating step (vitrification step), in order to stabilize the outer diameter, it is apparently important to maintain the temperature in the range of 1400°C to 1480°C (preferably 1400°C to 1440°C) for 70 minutes or more (preferably 100 minutes or more, and more preferably 150 minutes or more) for preventing elongation and for stabilizing the outer diameter.

Although the vacuum level in the furnace is set to 10 Pa in the examples,

a lower level may be desirable in order to prevent bubbles from remaining in the glass article. The level may be 9 Pa or 8 Pa.

The method of the present invention is effective in reducing the variation in outer diameter, when weight of the glass article is high, particularly when the weight is 50 kg or more.

Table 1: TREATMENT CONDITIONS AND OUTER-DIAMETER VARIATION IN THE OBTAINED GLASS ARTICLE

		Example 1a		Comparative Example 1a	
		Temperature (°C)	Time (min)	Temperature (°C)	Time (min)
First Heating Step	Degassing step	1300	60	1300	60
	Thermal Shrinking Step	1350	50	1350	50
Second Heating Step		1420	100	1500	60
Outer-Diameter Variation (mm)		±0.5		±4.5	

(Example 2a)

A soot preform 1 having the same size as that used in Example 1a was vitrified using the same equipment under the same temperature conditions as those in Example 1a. In this example, however, the temperature control during the vitrification step was performed by determining the temperature at the furnace tube 3 using the pyrometer 18 which measures the temperature at the outer surface of the furnace tube inside of the vacuum sintering furnace. The obtained glass article was measured and the results showed that the glass article had superior quality and a slight variation in outer diameter, i.e., the outer diameter over the entire effective length of 1400 mm was 90 ±0.7 mm (outer-diameter variation rate ±0.78%). These results show that the temperature at the furnace tube may be measured without causing any

problem instead of measuring the temperature at the surface of the soot preform 1. The temperature of the furnace tube is easier to measure.

(Example 2b)

A soot preform having the same size as that used in Example 1c was vitrified using the same equipment under the same temperature conditions as those in Example 1c. The obtained glass article was measured and the results showed that the glass article had superior quality, i.e., the outer diameter over the entire effective length of 1400 mm was 150 ±1.5 mm (outer-diameter variation rate ±1.0%).

(Example 3a)

A soot preform 1 having the same size as that in Example 1a was vitrified as in Example 1a using a vacuum sintering furnace of the same type as that shown in Fig. 3, the furnace having the heaters 4 divided into three units, i.e., an upper heater unit 4-1, a middle heater unit 4-2, and a lower heater unit 4-3 so as to allow independent control therein.

The soot preform 1 having an outer diameter of 200 mm and an effective length of 1560 mm was used. While maintaining the temperature in the vacuum sintering furnace at 400°C, the soot preform 1 was inserted into the furnace tube 3. The furnace was hermetically sealed with the upper cover 15 and the pressure in the furnace was reduced to 10 Pa. In this state, the surface temperature of the entire soot preform 1 was increased to 1300°C at a rate of 10°C/min and was maintained thereat for 60 minutes so as to degas the gas remaining in the soot preform 1 (degassing step).

The surface temperature of the soot preform 1 was then increased to 1350°C at a rate of 10°C/min, and was maintained thereat for 50 minutes (thermal shrinking step).

Next, the surface temperature at the middle of region A of the soot preform 1, the region that is significantly affected by the upper heater unit 4-1, was increased to 1400°C at a rate of 5°C / min, the surface temperature at the middle of region B significantly affected by the middle heater unit 4-2 was increased to 1420°C at a rate of 7°C / min, and the surface temperature at the middle of region C significantly affected by the lower heater unit 4-3 was increased to 1440°C at a rate of 9°C / min. The temperatures were maintained thereat for 100 minutes to completely vitrify the soot preform (vitrification step). The approximate temperature distribution during this step is shown in Fig. 3.

Heating by the heaters was discontinued so as to allow the temperature to decrease and so as to cool the glass article (cooling step), and the product was removed at 600°C.

The outer diameter of the obtained glass article was measured, and the results showed that the glass article had superior quality with little variation in outer diameter, i.e., the outer diameter over the entire effective length of 1405 mm was 90 ±0.1 mm (outer-diameter variation rate ±0.11%).

(Example 3b)

In Example 3a, the control of the surface temperature of the soot preform 1 was performed by determining and controlling the surface

temperature of the furnace tube 3 corresponding to each heater unit. Satisfactory quality was obtained as in Example 3a (the variation in the outer diameter over the entire effective length of 1417 mm was 90 ±0.3 mm (outer-diameter variation rate ±0.33%)).

(Example 3c)

Instead of the soot preform 1 of Example 3a, a composite preform having the same size as that in Example 3a and having a SiO_2 porous glass layer formed, by the VAD method, around a transparent glass rod comprising a central portion doped with Ge and a pure SiO_2 layer formed around the central portion, was used. The vitrification was performed as in Example 3a and satisfactory quality was also achieved.

(Example 3d)

The thermal-shrinking step at a temperature of 1350°C performed in Example 3a was omitted. Satisfactory quality was also obtained.

(Example 3e)

A soot preform 1 having the same size as that in Example 1c was used instead of the soot preform 1 in Example 3a. The vitrification step was performed as in Example 3a except that the holding time was 180 minutes. Satisfactory quality was obtained, i.e., the outer diameter over the entire effective length of 1390 mm was 150 ±0.7 mm (outer-diameter variation rate ±0.46%).

(Example 3f)

In Example 3e, the control of the surface temperature of the soot

preform 1 was performed by determining and controlling the surface temperature of the furnace tube 3 corresponding to each heater unit. Satisfactory quality was obtained as in Example 3a (the variation in the outer diameter over the entire effective length of 1400 mm was 150 ±1.0 mm (outer-diameter variation rate ±0.66%))

(Example 3g)

A soot preform 1 having an outer diameter of 365 mm, an effective length of 1560 mm, and a weight of 80 kg was vitrified by using the same equipment under the same conditions as in Example 3e. The size of the obtained glass article was measured and the results showed that the outer diameter over the entire effective length of 1470 mm was 163 ±1.5 mm (outer-diameter variation ±0.92%).

(Comparative Example 2)

A soot preform 1 having the same size as that used in Example 3g was vitrified using the same equipment as that in Example 3e under the conditions below. That is, while maintaining the temperature in the vacuum sintering furnace at 400°C, the soot preform 1 was inserted into the furnace tube 3, the furnace was hermetically sealed with the upper cover 15, and the pressure in the furnace was reduced to 10 Pa. In this state, the surface temperature of the entire soot preform 1 was increased to 1300°C at a rate of 10°C/min and was maintained thereat for 60 minutes so that the gas remaining in the soot preform 1 was thoroughly degassed (degassing step).

Then the surface temperature of the soot preform 1 was increased to

1350°C at a rate of 5°C/min, and was maintained thereat for 50 minutes (thermal-shrinking step).

Then the surface temperature of the soot preform 1 was increased at a rate of 15°C/min until the surface temperature of the entire soot preform 1 reached 1500°C. The temperature was maintained for 60 minutes to complete vitrification (vitrification step). Then heating by the heaters was discontinued so as to allow the temperature to decrease, and the product was removed at 600°C. The size of the obtained glass article was measured and the results showed that the glass article had a large variation in outer diameter in the longitudinal direction, i.e., the outer diameter over the entire effective length of 1660 mm was 90 ±4.5 mm (outer-diameter variation ±4.43%).